# **Reactions of Tetraethoxysilane Vapor on Polycrystalline Titanium Dioxide**

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The reactions of tetraethoxysilane (TEOS) vapor on dehydroxylated and water predosed polycrystalline TiO<sub>2</sub> were studied by Fourier transform infrared spectroscopy (FTIR) and temperature-programmed desorption (TPD). Exposure at 300 K leads to dissociative adsorption producing a monoethoxysilyl ligand and surface ethoxide species. The ethoxide ligands react and desorb in the range 450-650 K as gas phase ethanol and ethylene, while the monoethoxysilyl ligand decomposes at  $\sim 650$  K to gas phase ethanol and ethylene and surface bound SiO<sub>2</sub>. Dissociation of TEOS on TiO<sub>2</sub> is not affected by water predose; although, a greater amount of ethanol is produced in the gas phase at 550-650 K, and the SiO<sub>2</sub> which is formed exhibits vibrational features characteristic of a hydroxylated species. TEOS chemistry on TiO<sub>2</sub> was compared to the adsorption and reaction of ethanol on the same surface. Adsorption of ethanol at 300 K yielded surface ethoxide species which desorbed in two states as the parent alcohol and ethylene; desorption was also centered at 450 and 650 K. These results complement and supplement our previous study of TEOS on a TiO<sub>2</sub>(110) single crystal surface.

## I. Introduction

Silane coupling agents (SCA) are frequently used in a variety of chemical industries, primarily to provide bonding between dissimilar phases. Alkoxy functional silanes were originally utilized within polymer technologies as adhesion promoters, cross-linkers, and hydrophobes in efforts to solve the problems of peeling and penetration due to prolonged exposure to heat, cold, moisture, and chemical attack in the paint, ink, adhesive, water repellent, and related polymer industries.<sup>1,2</sup> SCAs have also found use as protective layer coatings, electronic sensors, chemically modified electrodes, thin film optics,<sup>3</sup> and as antireflection coatings.<sup>4,5</sup> More recently, needs in the microelectronics industry have stimulated the use of alkoxysilanes as gaseous precursors for the low-temperature growth of SiO<sub>2</sub> dielectric layers by chemical vapor deposition (CVD).<sup>6–8</sup>

Within the microelectronics industry, SCAs are gaining popularity for CVD of SiO<sub>2</sub> since alkoxysilanes incorporate both Si and O in a single source molecule and are typically less hazardous than traditional vapor phase silicon sources, such as silanes and chlorosilanes.<sup>6</sup> In the manufacture and fabrication of integrated circuits, SiO<sub>2</sub> is frequently used for intermetal isolation dielectrics, for gates in FET devices, and as passivation layers.<sup>7</sup> In high-performance integrated circuits, multilevel interconnect technology requires both deposition of a metal layer (normally Al) as a conduction path and deposition of a dielectric material between metal layers as an insulator.<sup>7</sup> Since the dielectric must be deposited on sharp metal lines without degradation or chemical reaction of the metal, the processing temperature is normally limited to <700 K.8 For these applications, good step coverage is of fundamental importance as well as filling small gaps between metal lines with void-free dielectric oxide.<sup>7</sup> Films deposited from tetraethoxysilane, or TEOS, exhibit good step coverage and thickness uniformity, as well as a low defect density and a low (compressive) film stress.9 Thus, TEOS has become the precursor of choice for vapor deposition of SiO<sub>2</sub>.<sup>6,9-12</sup>

Until recently, silanization of a surface was thought to occur through interaction of the alkoxy group in a SCA with adsorbed surface hydroxyl groups to form a surface–O–Si linkage and byproduct water.<sup>1,2,13</sup> However, we have recently shown that TEOS readily interacts with a TiO<sub>2</sub>(110) single-crystal surface and forms surface-bound SiO<sub>2</sub> *independent* of surface water or hydroxyl concentration.<sup>14</sup> Others have deposited SiO<sub>2</sub> by the adsorption and decomposition of TEOS on clean Si(100) and amorphous silica<sup>15,16</sup> and have observed silane coupling reactions by exposure of alkoxysilanes to severely dehydroxylated SiO<sub>2</sub>.<sup>15,17,18</sup> In addition, trimethoxysilane (TMS) was shown to form surface–O–Si bonds with an MgO(100) surface in the absence of surface hydroxyls.<sup>19,20</sup>

In our prior study<sup>14</sup> of the adsorption and reactions of TEOS vapor on clean and water (D<sub>2</sub>O) predosed TiO<sub>2</sub>(110), we found that the molecule sticks with a probability near unity at 130-300 K. At low coverages, TEOS dissociates upon heating, while at higher coverages, some desorbs. On the water- and hydroxylfree surface, the dissociation reaction occurs rapidly between 200 and 350 K, with the initial products being  $Si(OEt)_{x,s}$  plus  $(4 - x)OEt_s$  (where Et represents the C<sub>2</sub>H<sub>5</sub> group). The structure of the surface silyl ligand was intentionally left ill-defined, because we were unable to determine the stoichiometry of the dissociation reaction by TPD or X-ray photoelectron spectroscopy (XPS), due to water contamination. The OEt ligands, whether attached to Ti or Si atoms, decompose at  $\sim$ 650 K via  $\beta$ -hydrogen elimination to yield ethylene gas and surface-bound hydrogen, which rapidly attaches to another OEt ligand, yielding ethanol gas. By 700 K, the net products evolved are equal amounts of ethylene and ethanol gas (two molecules of each per dissociated TEOS molecule), while SiO<sub>2</sub> remains on the surface. With predosed D<sub>2</sub>O, quantitative TPD and XPS showed that the initial reaction leads to Si(OEt)2,s plus 2OEts, which are bound to Ti cations. However, the OEts produced now reacts with  $D_2O_s$  and/or  $OD_s$  to give an EtOD peak in the TPD spectrum at  $\sim$ 350 K. The amount of TEOS which dissociates is nearly doubled when D<sub>2</sub>O is present in high coverages. This is attributed to the fact that the D<sub>2</sub>O enhances elimination of OEt<sub>s</sub> (as EtOD), thus creating more free sites to accommodate dissociation products. The Si(OEt)<sub>2,s</sub> species is much less reactive with water than OEts and will remain on the surface to  $\sim 600$  K, irrespective of water predose.

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In this paper we investigate further the effects of surface water and hydroxyl concentration on the formation of SiO<sub>2</sub>. The adsorption and decomposition of TEOS on *polycrystalline* TiO<sub>2</sub> were studied using Fourier transform infrared spectroscopy (FTIR) and temperature programmed desorption (TPD) and is presented in section IIIA. By comparison with ethanol (EtOH) adsorption (section IIIB), we have determined the nature of the surface silyl ligand formed by dissociative adsorption of TEOS on the hydroxyl-free TiO<sub>2</sub> surface. IR assignments for all peaks are made and discussed in section IIIC. In section IV, we discuss pertinent surface reactions and propose a mechanism for TEOS reactions on dehydroxylated and water predosed polycrystalline TiO<sub>2</sub> surfaces.

#### **II. Experiment**

All IR and TPD experiments were performed in a stainless steel vacuum chamber with a base pressure of  $1.3 \times 10^{-6}$  Pa  $(1 \times 10^{-8} \text{ Torr})$ , described previously.<sup>21</sup> The system was equipped with a turbomolecular pump, quadrupole mass spectrometer, an ion pump, an ion gauge, a capacitance manometer, and a stainless steel gas handling manifold incorporating a leak valve and ballast. Ethanol, TEOS, and H<sub>2</sub>O were dosed from glass vials attached to the gas handling manifold. The chamber was mounted partially within, and externally O-ring sealed to, the sample compartment of a Bruker FTIR (Billerica, MA) system, such that the entire IR beam path could be evacuated. Dual O-ring sealed, differentially pumped KBr windows were employed to pass the IR beam through the high-vacuum chamber, and the sample was moved in and out of the IR beam path with a bellows assembly. IR data were recorded from 4000 to 500 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>, using a KBr beam splitter and a DTGS detector; each spectrum was the average of 64 scans. For each spectrum, a new reference spectrum, with the sample out of the beam path, was taken to calculate absorbance and eliminate the effects of background changes (if any), such as deposition on the KBr windows. All of the FTIR spectra presented here (except those of vapor phase EtOH and TEOS) were obtained by subtracting the spectrum of the clean TiO<sub>2</sub> substrate from the spectrum taken after exposure to either ethanol or TEOS and the indicated heat treatment. Subtracted spectra were not normalized before subtraction; however, some of the subtracted spectra presented here were base line leveled. This was done in order to account for the sloping background of the raw spectra that arose occasionally as a result of the substrate undergoing different light scattering losses.<sup>22</sup> Neither the subtraction or base line leveling procedures affected the IR peak positions or relative peak intensities. The thermal desorption system used in TPD experiments consisted of a UTI (San Jose, CA) quadrupole mass spectrometer interfaced to an instrument computer and was capable of monitoring up to 10 masses simultaneously. Temperature was controlled with a Eurotherm (Reston, VA) controller, linked to a power supply, which ramped the sample temperature linearly at 1 K/s.

Polycrystalline TiO<sub>2</sub> (Degussa AG; Frankfurt, FRG) was used as-received. Degussa TiO<sub>2</sub> has a reported BET surface area of 50 m<sup>2</sup>/g and an average particle diameter of 20-30 nm;<sup>23</sup> this titanium dioxide has primarily the anatase structure (70-90%).<sup>23,24</sup> Trace metallic impurities (Mg, Si, Al, Sn, and Cu) have been reported previously for this powder.<sup>25</sup> Fresh samples were prepared by hand-pressing the TiO<sub>2</sub> powder with a glass slide into a tantalum mesh which was clamped between two stainless steel arms connected to the power feedthroughs. In this way, the mesh served as a resistive heating element. A chromel-alumel thermocouple was spot-welded to the top center portion of the mesh to monitor temperature. All FTIR spectra presented here were obtained at room temperature.

Dehydrated ethanol (200 proof) was obtained from Midwest Grain Products Company (Pekin, IL), and high-purity TEOS, distilled in quartz, was obtained from Petrarch Systems (Bristol, PA). Water was purified by reverse osmosis and passed through a NANOPure (Barnstead; Dubuque, IA) system such that the resistance was at least 18 M $\Omega$ . Ethanol, TEOS, and water were further purified before dosing by several freeze-pump-thaw cycles. IR and mass spectra of ethanol and TEOS in the vapor phase agreed well with published standards,26-28 and no impurities were detected. Extra dry oxygen (Matheson Gas; Secaucus, NJ) had a purity of at least 99.6% and was used asreceived. The gas handling system was purged with dry nitrogen prior to each exposure series. Exposures at pressures less than 13.3 Pa (0.1 Torr) were achieved by dosing in a continuous flow mode at constant pressure through a small opening situated a few millimeters in front of and parallel to the front of the sample, while those at higher pressure were performed in a static back-filling mode. All exposures are reported in langmuirs (1 langmuir =  $1.3 \times 10^{-4}$  Pa·s =  $1 \times$  $10^{-6}$  Torrs).

In order to provide a hydroxyl-free surface, fresh TiO<sub>2</sub> samples were treated following previously published general procedures.<sup>22,29,30</sup> Samples were evacuated for 1 h at room temperature, treated in 13.3 Pa (0.1 Torr) of oxygen at 673 K for 1 h, and then cooled in vacuum for several hours. Lack of absorbance in the 3700-3000 cm<sup>-1</sup> range indicated a predominantly hydroxyl-free surface.<sup>22,29</sup> However, the small particles in the sample cause light scattering losses leading to a highly sloped spectrum with a poor signal-to-noise ratio in this region. This signal-to-noise problem is exacerbated when taking difference spectra, and as a result, a few hydroxyl groups may be present on the surface but not readily discernible in the data. Interpreting these spectra to represent hydroxyl-free samples does not alter the basic reaction chemistry or surface interactions we propose here. Occasionally, some isolated hydroxyl groups were not completely removed by the oxidation treatment,<sup>31</sup> and the interaction of these OH groups with EtOH and TEOS is discussed. After exposure to ethanol or TEOS, samples were regenerated by heating in vacuo to 673 K for 15 min (outgassing), followed by exposure to 26.6 Pa (0.2 Torr) of oxygen at 723 K for an additional 15 min. In this temperature range, the reported surface area of Degussa TiO<sub>2</sub> is not a strong function of outgassing temperature.<sup>25</sup> The regeneration treatment ensured a carbon- and hydroxyl-free sample with a vibrational spectrum identical to the fresh, dehydroxylated sample in the 4000-1200  $cm^{-1}$  region.

#### **III. Results**

A. Adsorption of TEOS on TiO<sub>2</sub>. In this section, we examine the adsorption of TEOS on polycrystalline  $TiO_2$  as probed by FTIR. IR data as a function of TEOS exposure are presented for dehydroxylated and water predosed surfaces. The behavior of IR features for saturated TEOS exposures on both types of surfaces as a function of annealing temperature are also discussed.

1. FTIR: Exposure Series. Figure 1A illustrates the C-H stretching region of the IR spectra as a function of increasing TEOS exposures to a dehydroxylated TiO<sub>2</sub> surface. All doses were performed consecutively at room temperature; the total exposure is shown in the figure. Exposures less than  $6 \times 10^3$  langmuirs did not show any significant intensity above the noise level. Peak assignments are given in Table 1 and are discussed in detail in section C. C-H stretching features are observed at 2981, 2938, and ~2900 cm<sup>-1</sup> (attributed to asymmetrical CH<sub>3</sub>, CH<sub>2</sub>, and combined symmetrical CH<sub>3</sub> and CH<sub>2</sub> vibrations, respectively; see section C) with greater intensity as the exposure



Figure 1. FTIR spectra as a function of TEOS exposure on partially hydroxylated  $TiO_2$  at 300 K, showing the (A) C-H stretching, (B) O-H stretching, and (C) low-wavenumber regions.

was increased. The C-H bending modes at 1675, 1560, 1480, 1445, 1400, and 1300 cm<sup>-1</sup> (not shown) showed increasing peak intensity with increasing TEOS exposure. Prior to regeneration, the sample was flashed to 1000 K during TPD, after which no features from the C-H stretching or bending regions remained, indicating these species had been removed from the surface.

The features at ~3690 and 3740 cm<sup>-1</sup> in Figure 1B represent consumption and production, respectively, of isolated hydroxyl groups on the sample. Since the IR spectra are *subtracted* absorbance spectra, positive peaks indicate production or growth of functional groups, while negative peaks indicate consumption of a particular functional group. In this case, a broad feature at 3690 cm<sup>-1</sup> on TiO<sub>2</sub> is characteristic of the antisymmetric stretching vibration from strongly bound (or chemisorbed) surface hydroxyl groups.<sup>22,32,33</sup> The sharp, intense peak at 3740

**TABLE 1: Vibrational Mode Assignments** 

-		peak positions (cm <sup>-1</sup> )			
	-	EtOH		TEOS	TEOS on
mode	EtOH <sub>(g)</sub>	on TiO <sub>2</sub>	TEOS(g)	on TiO <sub>2</sub>	H <sub>2</sub> O/TiO <sub>2</sub>
ν(OH)	3675				
$\nu_{\rm as}(\rm CH_3)$	2981	2973	2988	2981	2981
$\nu_{\rm as}({\rm CH_2})$	2981	2931	2940	2938	2938
$\nu_{\rm s}(\rm C-H)$	2900	2873	2907	$\sim 2900$	~2900
$\nu$ (Si-H)	$\sim 2207$				
$\nu$ (Ti $-O-Si$ )	1675	1675			
$\nu(-CO_2)$ or	1556	1560	1560		
$\nu$ (Ti $-O-Si$ )					
$\delta_{s}(CH_{2})$	1475	1480	1480		
$\delta_{as}(CH_3)$	1445	1445	1445	1445	1445
$\delta(CH_3)$	1400	1400	1400	1400	1400
$\delta_{\rm s}({\rm CH}_3)$	1244	1380			
$\delta(CH_2)$	~1360	1300	1300	1300	
$\nu(Si = O = C)$	1175	1175	1175		
$\rho(CH_2)$	1170				
v(C-O)	1125	1119	1113	1113	
$\nu(C-O)$	1100				
$\nu$ (Si-O-C)	1090	1090	1090		
$\nu(C-O)$	1060	1073			
$\nu(Si-O)$	1060	1060			
v(C-O)	1050				
$\nu(SiO_2)$	1040	1040			
$\nu(Si-O)$	~970	~970	~970		

 $cm^{-1}$  is typical of the hydroxyl vibration of Si-OH.<sup>5,13,16</sup> Thus, in Figure 1B, we observe a negative peak at  $\sim$ 3690 cm<sup>-1</sup> due to the consumption of isolated hydroxyl groups on TiO<sub>2</sub> as the surface is exposed to TEOS with the intensity of the negative peak increasing with exposure. Tedder et al.<sup>16</sup> and Hertl<sup>13</sup> have also observed consumption of isolated hydroxyl groups on silica upon dosing TEOS and methyltrimethoxysilane (MTMSi), respectively. While these authors observed the simultaneous production of associated hydroxyl groups with the consumption of isolated hydroxyl groups,<sup>13,16</sup> the absence of any  $\nu(O-H)$ features in the 3500-3000 cm<sup>-1</sup> region (not shown) suggests that associated hydroxyls are not formed. The peak at 3740  $cm^{-1}$  appears only after the hydroxylated TiO<sub>2</sub> sample is exposed to TEOS, flashed to high temperature, and regenerated. This peak is not observed when a *dehydroxylated* sample is exposed to TEOS; the assignment of this peak will be addressed in greater detail in the next section. After the regeneration procedure, no features remain in the  $\nu(O-H)$  or  $\nu(C-H)$ regions, except the sharp peak at 3740 cm<sup>-1</sup>. All other peaks behave similarly whether TEOS is dosed to a dehydroxylated or water predosed TiO<sub>2</sub> sample.

IR spectra showing the corresponding low wavenumber regions as a function of TEOS exposure on TiO<sub>2</sub> are shown in Figure 1C. In contrast to the  $\nu$ (C–H) and  $\delta$ (C–H) regions, a peak at 1040 cm<sup>-1</sup> appears after heating the sample for TPD and the regeneration procedure. At the highest exposures, this band is present only as a shoulder on the stronger, broad peak at ~1113 cm<sup>-1</sup>, while at lower exposures, only the broad peak at 1113 cm<sup>-1</sup> and the small peak at 1175 cm<sup>-1</sup> are observed. The peak at 1040 cm<sup>-1</sup> does not change whether TEOS was dosed to a dehydroxylated TiO<sub>2</sub> sample or one that had been water predosed. In addition to the peaks addressed here, a weak feature is discernible at ~2207 cm<sup>-1</sup> (not shown). This feature is also discussed below.

The peak at 1040 cm<sup>-1</sup> in Figure 1C is attributed to the stretching vibration of Si-O groups in a siloxane- or polymericlike network.<sup>26,34</sup> Vibrations of the Si-O bond at ~1050 cm<sup>-1</sup> are observed in methyl polysiloxanes and for degenerate symmetric vibrations of the SiO<sub>4</sub> group in liquid siloxanes.<sup>28,35</sup> In addition, siloxane bonds in tri-, tetra-, and pentasiloxane rings exhibit IR features in the range ~1020-1080 cm<sup>-1</sup>, depending on the amount of ring strain,<sup>28,36</sup> and a similar band in dimeric siloxane structures was assigned to Si-O-Si stretching vibrations.<sup>37</sup> A band near ~1100 cm<sup>-1</sup> is found in all forms of silica<sup>37</sup> and silica gels,<sup>34</sup> and the characteristic vibrational modes of SiO<sub>2</sub> are known to occur at frequencies 50–100 cm<sup>-1</sup> lower for films that are less than 50 Å thick.<sup>20,38</sup> Island formation or nonstoichiometric films may account for the frequency shift.<sup>38</sup> Previous reports have also noted that for less highly interlinked silica structures the Si-O bond is weakened, and the  $\nu$ (Si-O-Si) vibrational band at ~1100 cm<sup>-1</sup> shifts to lower frequency.<sup>39</sup> Thus, after flashing the TEOS exposed TiO<sub>2</sub> sample to 1000 K and regenerating, the peak at 1040 cm<sup>-1</sup> which emerges indicates a film of SiO<sub>2</sub> has formed on the surface.

2. FTIR: Successive Anneal. Infrared spectra taken as a function of temperature is an effective method to probe thermally induced surface chemistry.<sup>40</sup> In this method, the reaction at a given temperature is quenched, and the intermediate surface species may be examined spectroscopically at room temperature.<sup>40</sup> In order to quantify reaction products, identify any potential intermediates, and compare with EtOH experiments below, an infrared study of TEOS as a function of annealing temperature was undertaken. In these experiments, a water predosed ( $\sim 2.2 \times 10^8$  langmuirs) TiO<sub>2</sub> surface was exposed to TEOS ( $\sim 2.4 \times 10^8$  langmuirs) at room temperature. The surface was then raised to the desired temperature, held for 1 min, and then returned to 300 K where the IR data were obtained. The temperature of the heat treatment ranged from 300 to 850 K with a heating interval of 25 K; selected spectra are shown in Figure 2. In addition, a regeneration spectrum is included in the figure to show changes associated with regeneration.

Parts A and B of Figure 2 illustrate the C-H and O-H stretching regions, respectively, as a function of temperature for a TiO<sub>2</sub> sample sequentially exposed to water and TEOS at 300 K. The area under the C-H stretching peaks decreases monotonically as the sample is progressively heated. Peak areas were determined by a standard curve-fitting routine. A decrease in IR peak areas in the  $\nu$ (C-H) and  $\delta$ (C-H) regions (the latter is not shown) indicates fewer C-H groups are detected by IR as the temperature is raised and, in conjunction with our TPD results discussed below, suggests desorption of hydrocarbon species into the gas phase. The O-H stretching region in Figure 2B also undergoes changes with successive annealing. When TEOS is dosed to the sample, a negative peak at  $\sim$ 3690 cm<sup>-1</sup> and a broad positive peak at  $\sim$ 3300 cm<sup>-1</sup> (not shown) are observed. The former, as previously discussed, is due to the consumption of isolated hydroxyl groups on the TiO<sub>2</sub> surface, while the latter is due to the stretching vibration of hydrogenbonded OH groups of molecular water. The intensity of this latter feature increases with increasing water exposure (positive peak) but regularly decreases with increasing TEOS exposures (smaller positive peak). Upon heating to  $\sim$ 450 K, this feature disappears, and we observe H2O desorption in this temperature range during TPD (see below).

As the substrate is heated to ~450 K, the  $\nu$ (C-H) peak areas decrease by ~20% (Figure 2A); however, in this same temperature range, virtually no change is observed in the intensity of the negative peak at ~3690 cm<sup>-1</sup> (Figure 2B). Only a slight loss of the  $\nu$ (C-H) peak areas is seen between 450 and 550 K, while the negative feature at ~3690 cm<sup>-1</sup> has disappeared, indicating that most of the isolated OH groups that were initially consumed by the adsorption of TEOS have been replaced by 550 K. As the sample is further heated to 650 K, the  $\nu$ (C-H) peak areas decrease by a total of 54%, and by 750 K, only ~15% of the original peak area remains. Peak area losses at 450 and 650 K correspond well with quantitative TPD below. The sharp Si-OH peak at 3738 cm<sup>-1</sup>, which is not



Figure 2. FTIR spectra as a function of temperature for a  $\sim 2.4 \times 10^8$  langmuir exposure of TEOS to water predosed ( $\sim 2.2 \times 10^8$  langmuirs) TiO<sub>2</sub> at 300 K, showing the (A) C-H stretching, (B) O-H stretching, and (C) low-wavenumber regions. The z axis in (C) represents the processing stage, as described in the text.

initially present after dosing, appears only as the sample is heated above 650 K. The intensity of this peak decreases slightly as the sample is heated from 750 to 850 K and is shifted by  $\sim 2 \text{ cm}^{-1}$  to higher frequency. By 850 K, the area under the  $\nu(C-H)$  peaks has decreased to less than 10% of that at dosing. The decrease in peak areas of the C-H bending region (not shown) exhibits similar behavior. We did not observe any significant variation in the  $\nu(C-H)$  or  $\delta(C-H)$  peak positions as a function of temperature. After the sample is regenerated, no features remain in the  $\nu$ (C-H) region, but the Si-OH peak at 3740 cm<sup>-1</sup> has nearly doubled in intensity.

Figure 2C shows the corresponding low-wavenumber region of the IR spectra of TEOS on water predosed TiO<sub>2</sub> as a function of temperature. The z axis represents the progression through processing stages. Stages 1-3 are IR spectra of increasing water doses to the TiO<sub>2</sub> (total exposures of  $1 \times 10^7$ ,  $6 \times 10^7$ , and  $\sim 2.2 \times 10^8$  langmuirs), and spectra 4–6 are increasing TEOS doses (total exposures of  $1 \times 10^7$ ,  $1.1 \times 10^8$ , and  $\sim 2.4 \times 10^8$ langmuirs). Spectra 7-28 represent heat treatments at temperatures of 325-850 K for 1 min, followed by IR data acquisition at 300 K, while the final spectrum was taken after the regeneration treatment. Spectra 1-3 show no major absorption features, since IR features due to water adsorption are concentrated in the 3800-3000 and 1700-1600 cm<sup>-1</sup> regions, at higher frequency than those illustrated here. The  $\nu$ (Si-O),  $\nu$ (C-O), and  $\nu$ (Si-O-C) peaks at 1175, 1113 (with shoulders at  $\sim 1090$  and 1060 cm<sup>-1</sup>), and  $\sim 970$  cm<sup>-1</sup> are observed as TEOS is dosed (spectra 4-6). Initially, as the sample is heated to 325 K (spectra 7), the broad peak at 1113  $cm^{-1}$  narrows, and the shoulders at ~1090 and 1060 cm<sup>-1</sup> become more defined. In contrast to the C-H stretching region (Figure 2A), the peaks in the low-wavenumber region do not monotonically decrease with heat treatment. In fact, only about 30% of the initial peak area (spectra 6) is lost by heating to 450 K, with no further losses in peak area as the sample is heated to increasingly higher temperatures, indicating that most of the functional groups in this spectral region are retained throughout the annealing process and the Si-O linkages remain intact. The peak at  $\sim 1060 \text{ cm}^{-1}$  broadens during heating from 300 to  $\sim 650$ K, where the silica peak at 1040  $\text{cm}^{-1}$  emerges. By 750 K, the fwhm of this peak has decreased, and the peaks at 1113 and 1090 cm<sup>-1</sup> have become only shoulders on this dominant new peak. Recall that at this same temperature the  $3740 \text{ cm}^{-1}$  peak also appears (Figure 2B). Only the features at 3740 and 1040 cm<sup>-1</sup> remain after the sample is regenerated. A prior IR and Raman study comparing TEOS gels with fused quartz also indicated similar changes in peak positions and relative peak intensities as the gel transformed to a glass by a hydrolytic polycondensation process, where new Si-O-Si bonds were formed as a consequence of thermal treatment.<sup>34</sup>

Although Figure 2 shows specific IR spectra for TEOS exposed to a *water predosed* TiO<sub>2</sub> surface as a function of temperature, parts A and C of Figure 2 are also representative of the heat treatment series for a *dehydroxylated* sample exposed to TEOS at 300 K, and peak areas in the  $\nu$ (C–H) and  $\delta$ (C–H) regions decrease with increasing temperature. There are no features in the  $\nu$ (O–H) region. The peak at 1040 cm<sup>-1</sup> also appears at ~750 K as in Figure 3C. In addition, the  $\nu$ (Si–H) peak at ~2207 cm<sup>-1</sup> decreases with increasing temperature; 25% of the peak area is lost by 450 K and ~85% by 650 K. The behavior of this peak indicates that the  $\nu$ (Si–H) mode is degraded with increasing temperature and vanishes as SiO<sub>2</sub> is formed on the surface.

3. TPD. A typical TPD experiment involved simultaneously recording 10 masses (including some combination of m/e = 79, 74, 59, 45, 44, 31, 30, 29, 28, 26, 18, and 2) and then analyzing the mass desorption curves quantitatively. This analysis included corrections to the spectra for experimentally determined cracking patterns, ionization efficiency, and the transmission and electron multiplier gain of the mass spectrometer. Cracking patterns were experimentally measured for the following desorption products: acetaldehyde, CO<sub>2</sub>, diethyl ether, EtOH, and ethylene; the quadrupole manufacturer's cracking pattern data were used for acetylene, ethane, methane, butene, and methanol. The electron multiplier gain of the mass



**Figure 3.** TPD spectra showing normalized reaction product yield rate *versus* temperature for (A)  $1.1 \times 10^8$  langmuir exposure of TEOS to dehydroxylated TiO<sub>2</sub> at 300 K and (B)  $1.1 \times 10^8$  langmuir exposure of TEOS to the water predosed ( $\sim 2.2 \times 10^8$  langmuirs) surface at 300 K. As indicated, spectra for H<sub>2</sub>O and H<sub>2</sub> desorption in (A) and H<sub>2</sub> desorption in (B) are magnified by a factor of 2.

 TABLE 2: TEOS on TiO2 TPD Product Yield and Peak

 Temperatures

	low tem	low temperature high		temperature	
compound	yield	$T_{p}(K)$	yield	$T_{p}(K)$	
Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	0.024	406	0.042	601	
$C_2H_2$	5.24	413	3.64	662	
$C_2H_6$	0.98	419	1.88	678	
CH <sub>3</sub> CHO	0.09	420	0.42	666	
$CO_2$	0.23	420	1.11	666	
H <sub>2</sub> O	3.17	421	6.24	732	
$H_2$	3.58	429	9.73	684	
C <sub>2</sub> H <sub>5</sub> OH	13.20	431	19.90	652	
$(C_2H_5)_2O$	0.57	630			
$C_2H_4$	29.94	693			

spectrometer was estimated for  $H_2$  from a plot of gain vs m/e supplied by the manufacturer, such that a semiquantitative analysis of  $H_2$  desorption has been made. Thus, in Figure 3 we present the TPD data as desorption product yields, rather than relative m/e intensities. Areas of the product yield curves were found by fitting Gaussian peaks to the TPD spectra, with the low-temperature peak centered at ~425 K.

Parts A and B of Figure 3 illustrate TPD data for typical 1.1  $\times 10^8$  langmuir exposures of TEOS to dehydroxylated and water predosed ( $\sim 2 \times 10^8$  langmuir) TiO<sub>2</sub> surfaces, respectively. The major products (ethanol, ethylene, water, and hydrogen) are shown in the figure, while Tables 2 and 3 summarize the TPD product distributions, including minor desorption products, such as acetaldehyde, CO<sub>2</sub>, ethane, and acetylene. The data presented in the tables are the average of repeated experiments; "yield"

TABLE 3: TEOS on Water Predosed TiO<sub>2</sub> TPD Product Yield and Peak Temperatures

	low temperature		high temperature	
compound	yield	$T_{p}(K)$	yield	$T_{p}(K)$
Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	0.042	408		
$C_2H_2$	4.88	495		
$C_2H_6$	0.58	477		
CH₃CHO	0.10	436		
$CO_2$	0.26	436		
$H_2O$	32.21	434	7.64	730
$H_2$	8.92	449	2.34	650
C <sub>2</sub> H <sub>5</sub> OH	11.96	428	18.82	554
$(C_2H_5)_2O$	0.18	582		
$C_2H_4$	12.08	680		

represents the relative percent yield based on all desorption products and temperature ranges, and  $T_p$  is the peak desorption temperature. The major products desorb in two states: a low-temperature state, centered at ~425-440 K, and a high-temperature state. The high-temperature state is centered at ~650-680 K on the dehydroxylated surface and at ~550-650 K on the water predosed surface.

For TEOS decomposition on dehydroxylated TiO<sub>2</sub> (Figure 3A), the product ratio is 1:1.5:2.5  $\pm$  0.18 for ethanol in the low-temperature state: ethylene in the high-temperature state. No significant hydrogen or water desorption was observed in the low-temperature regime, with only a small amount of water desorption accounts for a negligible percentage of TPD products. Ethane desorption, as well as desorption of  $\alpha$ -hydrogen elimination products (such as acetaldehyde), was also negligible.

The TPD spectra of the major reaction products from exposures of TEOS to a water predosed TiO<sub>2</sub> sample, illustrated in Figure 3B, is qualitatively similar to that observed in Figure 3A, except for the high-temperature desorption of EtOH, which is shifted to ~555 K. The Gaussian curve fitted to the high-temperature TPD peak for ethanol desorption is very broad with significant contributions from the low temperature desorption state as well as an extended tail to higher temperatures. The product yield is 1:1.7:1 ± 0.13 of low-temperature ethanol:high-temperature ethanol:high-temperature ethanol:high-temperature ethylene, with water desorption accounting for ~40% of all desorption products. Again, only negligible desorption of molecular TEOS, ethane, and  $\alpha$ -hydrogen elimination products were observed from the water predosed sample.

**B.** Adsorption of EtOH on TiO<sub>2</sub>. In order to identify surface intermediates from TEOS decomposition on TiO<sub>2</sub>, comparison is made to EtOH adsorption and interaction on these surfaces. Results of FTIR and TPD experiments are presented in the following sections.

1. FTIR: Exposure Series. Figure 4 shows the IR spectra for increasing exposures of EtOH to TiO<sub>2</sub>; total exposures are given. Samples were flashed to 1000 K (with TPD) before the regeneration procedure. As for TEOS, exposures less than 6  $\times$  10<sup>3</sup> langmuirs did not show any significant intensity above the noise level. The major features in the O-H and C-H stretching regions (Figure 4, parts A and B) are the increasing intensity of the  $\nu$ (C-H) peaks and the consumption of isolated hydroxyl groups. Peaks are assigned to vibrational modes in Table 1, and mode assignments are discussed in section C. The  $\nu$ (C-H) peaks in Figure 4A intensify with increasing EtOH exposures, and at the highest exposures, some intensity at  $\sim 2900$  $cm^{-1}$  may be identified. The feature at ~3690 cm<sup>-1</sup> in Figure 4B represents consumption of surface OH groups. EtOH is known to displace water from TiO2,<sup>41</sup> although the reverse is not observed. Others have observed the consumption of isolated hydroxyl groups and production of hydrogen-bonded hydroxyl



Figure 4. FTIR spectra as a function of EtOH exposure on  $TiO_2$  at 300 K, showing the (A) C-H stretching and (B) O-H stretching regions.

upon dissociative adsorption of EtOH on TiO<sub>2</sub>;<sup>22,33</sup> however, we do not observe any features in the 3600-3400 cm<sup>-1</sup> region (not shown), where the characteristic stretches of hydrogenbonded OH groups are typically observed.<sup>22,25,30,32,33,42</sup> As expected, peaks in the C-H bending region (not illustrated) also show greater intensity as a function of increasing EtOH exposure.

Perhaps the most important characteristic of Figure 4 is the lack of absorbance features in the *regeneration* spectrum, obtained after TPD and regeneration. The lack of IR absorbance in the 4000-500 cm<sup>-1</sup> region of the subtracted spectrum indicates that the substrate has not undergone any irreversible changes by the adsorption of EtOH. Note also that the majority of the hydroxyl groups consumed by adsorption of EtOH on TiO<sub>2</sub> (Figure 4B) are replaced during the regeneration treatment, since the spectrum shows no negative intensity at ~3690 cm<sup>-1</sup>.

2. FTIR: Successive Anneal. The C-H stretching region is shown in Figure 5 for EtOH on TiO<sub>2</sub> as a function of temperature. EtOH was dosed at room temperature, and the sample was progressively heated in intervals of 25 K. The sample was held at the given temperature for 1 min before cooling to 300 K and acquiring the IR spectra; temperatures ranged from 300 to 850 K. The area under the  $\nu$ (C-H) peaks decreases monotonically as the sample is heated. TPD data presented below provides evidence that as the  $\nu$ (C-H) peaks decrease, surface hydrocarbon species are desorbing. We observe a loss of 25% of  $\nu$ (C-H) peak area by heating the sample to 450 K. Further heating the sample to 650 K results in a total loss of 70-75% of the peak areas, with additional product desorption. Neither a significant decrease in the peak areas nor major product desorption is observed between 450



Figure 5. FTIR spectra as a function of temperature for a  $\sim 1.1 \times 10^8$  langmuir exposure of EtOH to TiO<sub>2</sub> at 300 K, showing the C–H stretching region.



**Figure 6.** TPD spectra showing normalized reaction product yield rate of a  $\sim 1.1 \times 10^8$  langmuir exposure of TiO<sub>2</sub> to EtOH at 300 K. As indicated, spectra for EtOH, H<sub>2</sub>O, and H<sub>2</sub> desorption are magnified by a factor of 2.

and 550 K or between 650 and 750 K. The peaks in the  $\delta$ (C-H) and low-wavenumber regions (not shown) are also reduced with increasing temperature, and no additional peaks are observed from 4000 to 500 cm<sup>-1</sup>, indicating that ethoxide is the only species on the surface. The negative peak at ~3690 cm<sup>-1</sup>, showing consumption of isolated hydroxyl groups, does not vary to any extent with temperature, and as in Figure 4, a featureless IR spectrum results after regeneration of the sample in this region. Again, the absence of IR peaks after regeneration signifies that EtOH adsorption is reversible.

3. TPD. Figure 6 illustrates a typical TPD spectrum of the desorption products from a  $1.1 \times 10^8$  langmuir room temperature exposure of EtOH to TiO2. TPD data were analyzed as for TEOS. No changes in product distribution or desorption temperature were observed for adsorption on clean TiO<sub>2</sub> or on samples that had been previously exposed to EtOH and/or TEOS and regenerated. In addition, the TPD spectra did not vary to any significant extent with increasing surface hydroxyl concentration. Ethylene is the primary desorption product in the high-temperature state. The product yield ratio is  $1:1:2 \pm 0.23$ for the desorption of low temperature ethanol:high-temperature ethanol:high-temperature ethylene. These data are qualitatively in agreement with previously published studies of EtOH adsorption on anatase powder, where ethylene was observed as the primary high-temperature desorption product,<sup>29</sup> and on rutile,<sup>33</sup> as well as a similar study on a {011}-faceted TiO<sub>2</sub>-(001) single crystal.43



Figure 7. FTIR spectra of TEOS (a) on dehydroxylated and (b) on water predosed polycrystalline TiO<sub>2</sub> (exposures at 300 K) and (c) TEOS vapor at  $1.3 \times 10^2$  Pa (1 Torr). As indicated, spectra (a) and (b) are magnified by factors of 10 and 7, respectively, to provide a better comparison with the gas phase spectrum.

C. Vibrational Mode Assignments. In this section FTIR vibrational mode assignments are discussed in detail. The general reader will not lose continuity by skipping ahead to the Discussion section. However, vibrational mode assignments are of importance to spectroscopists and others studying similar systems and are included for completeness.

1. TEOS on  $TiO_2$ . Shown in Figure 7 are the infrared spectra for TEOS on dehydroxylated TiO<sub>2</sub> (curve a), TEOS on water predosed TiO<sub>2</sub> (curve b), and TEOS vapor (curve c). Figure 7a is the IR spectrum resulting from a  $2.1 \times 10^8$  langmuir exposure of TEOS at 300 K. Major C-H stretching peaks are seen at 2981, 2938, and  $\sim$ 2900 cm<sup>-1</sup>, while major C-H bending peaks are observed at 1480, 1445, 1400, and 1300 cm<sup>-1</sup>, as well as two broad bands at 1675 and 1560  $cm^{-1}$ . In the lowwavenumber region of the spectrum, we also observe vibrational bands at 1175, 1113, and  $\sim 970$  cm<sup>-1</sup>, with the broad peak at 1113 cm<sup>-1</sup> showing two low-frequency shoulders at 1090 and 1060 cm<sup>-1</sup>. In addition, a small peak is discernible at  $\sim 2207$ cm<sup>-1</sup>. Previous FTIR studies of TEOS on amorphous silica utilized the vibrational spectra of adsorbed EtOH and CH<sub>3</sub>CD<sub>2</sub>-OH in making vibrational mode assignments;<sup>16</sup> we have correlated the peaks in Figure 7 with vibrational modes (Table 1), based on this prior study,<sup>16</sup> as well as by comparison with reported spectra<sup>26,28,34,35</sup> of liquid TEOS and the spectra of EtOH adsorbed on TiO<sub>2</sub>, discussed below.

Peaks in the C-H stretching region of TEOS exposed TiO<sub>2</sub> (Figure 7a) at 2981 and 2938 cm<sup>-1</sup> are assigned to the antisymmetric stretching modes of the CH<sub>3</sub> and CH<sub>2</sub> groups,  $v_{as}(CH_3)$  and  $v_{as}(CH_2)$ , respectively.<sup>3,35,39</sup> At low exposures (Figure 1A), the peak at  $\sim 2900 \text{ cm}^{-1}$  is assigned to the combined symmetric stretches of the CH<sub>3</sub> and CH<sub>2</sub> groups,  $v_{\rm s}$ (C-H). This is consistent with our observations of the C-H stretching modes of EtOH on TiO<sub>2</sub>, as well as a prior assignment<sup>22</sup> for EtOH adsorbed on pure anatase, where only one symmetric stretching vibration was observed. Others, however, have observed two symmetric stretching vibrations assigned specifically to  $v_s(CH_3)$  and  $v_s(CH_2)$ , at 2936 and 2905 cm<sup>-1</sup> for TEOS on amorphous silica,<sup>16</sup> at 2939 and 2909 cm<sup>-1</sup> for EtOH on amorphous silica,<sup>16</sup> at 2874 and 2850 cm<sup>-1</sup> for EtOH on a Pt/TiO<sub>2</sub> catalyst,<sup>44</sup> and at  $\sim$ 2870 and  $\sim$ 2850 cm<sup>-1</sup> for many liquid phase organic compounds.<sup>45,46</sup> Exposure of an oxidized aluminum surface to TEOS yielded only two peaks in the C-H stretching region at 2977 and 2886 cm<sup>-1</sup>, corresponding to  $v_{as}(CH_3)$  and  $v_s(CH_3)$ ,<sup>3</sup> although some intensity was also present at ~2940 cm<sup>-1</sup>, which may be attributed to  $v_{as}(CH_2)$ . The assignment of the peak at  $\sim 2900 \text{ cm}^{-1}$  for low coverages

to the combined stretching of the CH<sub>3</sub> and CH<sub>2</sub> groups is based on the fact that, at low exposure, the signal-to-noise ratio is too low to resolve the two features.<sup>22,33,41</sup> At higher exposures (Figure 2A), however, two peaks are resolved at 2905 and 2874 cm<sup>-1</sup> and assigned to  $\nu_s$ (CH<sub>3</sub>) and  $\nu_s$ (CH<sub>2</sub>).

Peaks in the C-H bending region at 1480, 1445, and 1400 cm<sup>-1</sup> are well-cited in the literature and are attributed to the symmetric bend (scissoring) of the CH<sub>2</sub> group<sup>16</sup>,  $\delta_s$ (CH<sub>2</sub>), an antisymmetric CH<sub>3</sub> bend,  $^{16,34-36} \delta_{as}$  (CH<sub>3</sub>), and a symmetric deformation (wag) of the CH<sub>3</sub> group,  $^{3,16,20,34-36}$   $\delta_s$ (CH<sub>3</sub>), respectively. The broad bands at 1560 and 1675 cm<sup>-1</sup> are present in previously published vapor and liquid phase IR spectra,<sup>26,28,34,36</sup> but vibrational modes were not assigned. The peak at 1560 cm<sup>-1</sup> is likely related to the antisymmetric stretching mode of the CO<sub>2</sub> group of a surface acetate species, as observed for ethanol exposed TiO<sub>2</sub> and discussed below. However, peaks at 1545 and 1636 cm<sup>-1</sup> were also observed in the mixed oxide TiO<sub>2</sub>/SiO<sub>2</sub> and attributed to Brønsted acid sites originating from the Ti-O-Si linkage.<sup>47</sup> In Table 1 we have assigned the band at 1675 cm<sup>-1</sup> to a Ti-O-Si vibration, while the peak at 1560  $cm^{-1}$  may be due to the acetate-like CO<sub>2</sub> vibrational mode and/or a Ti-O-Si linkage.

Vibrational bands in the low wavenumber region are assigned primarily to  $\nu(C-O)$ ,  $\nu(Si-O)$ , and  $\nu(Si-O-C)$ . In the IR region between  $\sim$ 1111 and 1000 cm<sup>-1</sup>, SCAs typically have very strong vibrational bands.<sup>28,46,48</sup> For disiloxanes, this band may be found in the region  $\sim 1124-1020$  cm<sup>-1</sup>, while for tri- or tetrasiloxanes this band may split into two or more overlapping components.<sup>28</sup> In particular, the infrared spectra of ethoxysilanes (such as triethylethoxysilane, triethoxyethylsilane, and TEOS) show a cluster of bands in the 1055-1120 cm<sup>-1</sup> region.<sup>37</sup> In addition, the substitution of C for Si in a siloxane structure leads to only slight modifications of the infrared spectra.<sup>37</sup> In Figure 7a, we observe the overlap of all or some of the  $\nu(Si-$ O),  $\nu$ (C-O),  $\nu$ (Si-O-C),  $\delta$ (C-H), and  $\nu$ (C-C) modes. However, by comparison with previously published spectra, we can assign the vibrational band at 1175 cm<sup>-1</sup> and the shoulder at 1090 cm<sup>-1</sup> to the doublet stretching vibration of the Si-O-C functionality,<sup>3</sup> while the peak at  $\sim 1113 \text{ cm}^{-1}$  may be attributed to the stretching frequency of the C-O bond.<sup>20,49</sup> These vibrational mode assignments are in agreement with those made by researchers studying photoacoustic FTIR to measure the degree of curing in a polymeric network by reaction of TEOS and poly(dimethylsiloxane) (PDMS); bands at 1076, 1067, and 1057  $cm^{-1}$  were assigned to the C-O stretch of ethanol produced in the cross-linking reaction.<sup>48,50</sup> A highresolution electron energy loss spectroscopy (HREELS) study revealed a loss feature at  $\sim 1103$  cm<sup>-1</sup> for TEOS on Si(100)-2  $\times$  1 at 90 K, which was also assigned to the  $\nu$ (C–O) vibration.<sup>20</sup> Thus, we have attributed the feature at 1113  $cm^{-1}$  primarily to the  $\nu$ (C-O) vibrational mode. Finally, the features at 1060 and  $\sim 970 \text{ cm}^{-1}$  can be attributed to stretching interactions of the Si-O bond.<sup>3,34,35,39,51</sup> The band at  $\sim$ 970 cm<sup>-1</sup> may also include some vibrational contributions from the substrate in the form of Si-O-Ti bonds, since vibrational bands between ~1000 and 900 cm<sup>-1</sup> in mixed oxide silicates are typically due to Si-O-M vibrations (where M represents a metal atom).<sup>28,52</sup> Since the TiO<sub>2</sub> powder is opaque to IR radiation at less than  $\sim 900 \text{ cm}^{-1}$ , no features were detected from the formation of SiO<sub>4</sub> strained tetrahedral rings, which typically show absorbance features at 908 and 888 cm<sup>-1</sup> for SiO<sub>2</sub> networks or surfaces.<sup>53,54</sup> The Ti-O-Ti chain network absorbs at  $\sim 900 \text{ cm}^{-1}$  (the stretching mode of the Ti-O bond typically shows IR features at  $\sim 970-975$ cm<sup>-1</sup> in salts<sup>55</sup>); thus, vibrations in the substrate preclude investigation of adsorbate features at less than  $\sim 900 \text{ cm}^{-1}$ .

The peak at ~2207 cm<sup>-1</sup> in Figure 7a is not apparent in previously published spectra of molecular TEOS;<sup>3,26,28,34-36</sup> however, a peak at ~2100 cm<sup>-1</sup> was reported for TEOS deposition on Si(100)-2 × 1.<sup>20</sup> Vibrations at this frequency in silicon systems are assigned to the stretching frequency of Si-H bonds;<sup>20,26,36</sup> however, the absolute absorbance of the band at ~2200 cm<sup>-1</sup> for a compound such as triethoxysilane, SiH-(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, is approximately the same as for the  $\nu$ (C-H) bands<sup>26</sup> and is also intense for most organosilicon compounds.<sup>28</sup> Since the peak at ~2207 cm<sup>-1</sup> is less intense than the  $\nu$ (C-H) features in Figure 7a, fewer Si-H vibrations must be present for TEOS on TiO<sub>2</sub> than in these other systems. The nature of this peak will be discussed below.

Figure 7b illustrates the IR spectrum for a  $\sim 2.4 \times 10^8$ langmuir exposure of TEOS on a TiO<sub>2</sub> sample which had been previously exposed to  $\sim 2.2 \times 10^8$  langmuirs of water. Both water and TEOS were dosed at 300 K. Most of the major features in Figure 7b occur at the same frequency as those in Figure 7a and are attributed to the same vibrational modes (Table 1) as assigned above. The relative intensities and peak positions do not vary as a function of the water predose. A new, broad peak at  $\sim 3300 \text{ cm}^{-1}$  is observed in Figure 7b, while the peak at  $\sim 1100 \text{ cm}^{-1}$  is broader than on the dehydroxylated surface and the feature at  $\sim 2207 \text{ cm}^{-1}$  is not present. The feature at  $\sim 3300 \text{ cm}^{-1}$  in Figure 7b is attributed to the stretching vibration of associated, or hydrogen-bonded, hydroxyl groups resulting from the water predose.<sup>22,24,25,31-33,40,46</sup>

The IR spectra shown in Figure 7a,b for TEOS exposed TiO<sub>2</sub> did not show any significant changes in absorption intensity, peak position, or relative peak intensities after extended evacuation (~14 h). Additionally, as we will discuss below, we did not observe any significant desorption of the parent molecule in TPD. In light of these observations, as well as our prior study of the adsorption of TEOS on TiO<sub>2</sub>(110)<sup>14</sup> and other studies of SCA adsorption,<sup>3,4,6,16-20,56</sup> we can conclude that exposure of TEOS to TiO<sub>2</sub> at room temperature leads to dissociative adsorption, independent of the surface water or hydroxyl concentration. The mechanism for the adsorption and decomposition of TEOS on single-crystal TiO<sub>2</sub> was described in detail in our prior work,<sup>14</sup> and adsorption and decomposition of TEOS on polycrystalline TiO<sub>2</sub> are compared to EtOH adsorption below.

IR spectra of strongly adsorbed TEOS on polycrystalline TiO<sub>2</sub> (Figure 7a,b) may be compared to Figure 7c, which illustrates the vibrational spectrum for TEOS vapor. This spectrum was obtained at 300 K and a pressure of 133 Pa (1 Torr). Although Figure 7c is similar to Figure 7a,b, as well as the IR spectra of EtOH vapor (presented below), the C-H stretching peaks of vapor phase TEOS are observed at slightly higher frequencies (2988, 2940, and 2907 cm<sup>-1</sup>) as compared to the adsorbed species. A shift to higher frequency of the primary peaks is usually observed when comparing a gas phase IR spectra with that of an adsorbate, since the vibrations are not affected by substrate bonding.<sup>45</sup> Vibrational modes are assigned in Table 1; no differences in peak position are observed in the C-H bending region. Peaks at 1175 and 1090 cm<sup>-1</sup> are attributed to the  $\nu$ (Si-O-C) doublet,<sup>3</sup> at 1119 cm<sup>-1</sup> to  $\nu$ (C-O),<sup>19,49</sup> and at ~970 cm<sup>-1</sup> to a  $\nu$ (Si-O) mode.<sup>3,34,35,39,51</sup> The peaks at 1119 and 1090 cm<sup>-1</sup> have a smaller fwhm than those for the adsorbed species, since rotational motion is not restricted in the vapor phase.45

2. EtOH on TiO<sub>2</sub>. Shown in Figure 8a is the IR spectrum of a  $1.1 \times 10^8$  langmuir exposure of EtOH on TiO<sub>2</sub> at room temperature. This spectrum has been base line leveled and magnified by a factor of 7 for comparison with the gas phase FTIR spectra (curve b). In agreement with prior reports<sup>16,22,33,41,46</sup>



**Figure 8.** FTIR spectra at 300 K of (a) EtOH on polycrystalline TiO<sub>2</sub>, and (b) EtOH vapor at  $1.3 \times 10^3$  Pa (10 Torr). Spectra a is magnified by a factor of 7 to provide a better comparison with the gas phase spectrum.

and the gas phase IR spectrum,<sup>26,46</sup> major C-H stretching bands are observed at 2973, 2931, and 2873 cm<sup>-1</sup> and major C-H bending vibrations are seen at 1475, 1445, 1400, 1380, and  $\sim$ 1360 cm<sup>-1</sup> as well as a broad peak at 1556 cm<sup>-1</sup>. Additional bands are observed at 1125, 1073, and 1050 cm<sup>-1</sup>. Both highand low-frequency shoulders, at  $\sim 1170$  and 1100 cm<sup>-1</sup>, can be seen on the 1125  $cm^{-1}$  peak, indicating that more than one surface species may be contributing to this vibrational mode.<sup>40</sup> All of these major bands have been previously reported and are assigned to vibrational modes in Table 1. Peak positions and peak shapes for TiO<sub>2</sub> exposed to EtOH, as in Figure 8, are consistent with those reported in the literature for EtOH exposures to anatase,<sup>22</sup> rutile,<sup>33</sup> and amorphous silica.<sup>16</sup> As for the ethoxy ligands of TEOS at low exposure, the peaks at 2973, 2931, and 2873 cm<sup>-1</sup> are assigned to  $v_{as}$ (CH<sub>3</sub>),  $v_{as}$ (CH<sub>2</sub>), and the combined symmetric stretches of the CH<sub>3</sub> and CH<sub>2</sub> groups,  $v_{\rm s}({\rm C-H})$ , respectively. The latter assignment is made for low exposures, since the signal-to-noise level precluded us from resolving the  $v_s(CH_3)$  and  $v_s(CH_2)$  features clearly at these coverages. At higher exposures, the  $\nu_s(CH_3)$  and  $\nu_s(CH_2)$  modes are assigned to peaks at 2900 and 2873  $cm^{-1}$ .

In the C–H bending region, the peaks at 1475, 1445, and 1380 cm<sup>-1</sup> are well-cited in the literature; the former is assigned to the scissoring deformations of the CH<sub>2</sub> group,<sup>16,33,45,46</sup> and the latter two deformations are due to  $\delta_{as}$ (CH<sub>3</sub>). <sup>16,33,45,46</sup> The bands at 1400 and ~1360 cm<sup>-1</sup> may be attributed to the wagging deformations of the CH<sub>3</sub><sup>16</sup> and CH<sub>2</sub><sup>33</sup> functionalities. These bands may also be correlated with the weak, broad band at ~1556 cm<sup>-1</sup>. Vibrational bands have previously been observed at ~1550, 1370, and 1360 cm<sup>-1</sup> for formate on TiO<sub>2</sub>;<sup>24</sup> and the vibration at 1556 cm<sup>-1</sup> has been attributed to the antisymmetric CO<sub>2</sub> stretching mode of surface formate- or acetate-like groups.<sup>24,30,40,45,46,57,58</sup> TPD data (Table 4) shows that the exposure of TiO<sub>2</sub> to EtOH yields small percentages of acetaldehyde and CO<sub>2</sub> in the gas phase.

Vibrational bands in the low-wavenumber region of the IR spectrum for TiO<sub>2</sub> exposed to EtOH are also assigned in Table 1. Typically, the low-wavenumber region of an infrared spectrum may contain several coupled and overlapping vibrational modes for  $\nu$ (C-C),  $\nu$ (C-O), and  $\delta$ (C-H);<sup>45,46</sup> thus, without having studied the frequency shifts of these peaks by isotopic labeling, we assigned vibrational modes to these peaks, based upon previous assignments in the literature and the gas phase spectrum discussed below. Peaks at 1125, 1073, 1050, and 1100 cm<sup>-1</sup> have been assigned to the stretching frequency of the C-O functionality.<sup>33,44,46,48,50,59-61</sup> The C-C stretching vibration may also contribute intensity to these peaks, as this

 TABLE 4: EtOH on TiO2 TPD Product Yield and Peak

 Temperatures

	low temperature		high temperature	
compound	yield	T <sub>p</sub> (K)	yield	T <sub>p</sub> (K)
C <sub>2</sub> H <sub>2</sub>	4.19	438		
$C_2H_6$	0.42	439	1.43	674
CH <sub>3</sub> CHO	0.14	421	0.37	658
CO <sub>2</sub>	0.36	421	0.98	658
H <sub>2</sub> O	22.43	424	14.81	692
$H_2$	6.36	442	7.29	673
C <sub>2</sub> H <sub>5</sub> OH	9.04	430	7.00	650
$(C_2H_5)_2O$	0.31	648		
C <sub>2</sub> H <sub>4</sub>	1.40	423	23.52	678

mode is typically observed in the  $1200-1000 \text{ cm}^{-1}$  region.<sup>45,46,62,63</sup> Finally, the small feature at  $\sim 1170 \text{ cm}^{-1}$  in Figure 8a is attributed to the rocking motion of the CH<sub>2</sub> group.<sup>22,59,63</sup>

Presented for comparison, as Figure 8b, is the IR spectrum of gas phase ethanol, which exhibits strong absorption bands at 3675, 2981, 2900 cm<sup>-1</sup> and at 1445, 1400, 1244, and  $\sim$ 1060 cm<sup>-1</sup>. This spectrum was obtained at room temperature and a pressure of 133 Pa (10 Torr) and is in excellent agreement with reported spectra for gas phase ethanol.<sup>26,46</sup> Note that the IR spectrum of vapor phase EtOH (Figure 8b) also reveals much of the rotational fine structure.<sup>45</sup> The primary absorption bands have been studied previously<sup>16,33,45,46,61</sup> and are assigned to vibrational modes (Table 1). The peak at 3675 cm<sup>-1</sup> is assigned to the stretching frequency of the hydroxyl group, while the bands at 2981 and 2900 cm<sup>-1</sup> are attributed to the antisymmetric and symmetric C-H stretches, respectively.<sup>61</sup> The vibrations at 1445 and 1400 cm<sup>-1</sup> are due to the internal symmetric and antisymmetric CH<sub>3</sub> deformation modes, <sup>16,22,33,45,46</sup> while the peak at 1244  $cm^{-1}$  is assigned to the OH bending mode.<sup>40</sup> Finally, the strong band at 1060 cm<sup>-1</sup> is attributed to  $\nu$ (C-O).<sup>33,43</sup>

In agreement with previous researchers, 16,22,29,33,45,57,61 we find that exposing a metal oxide, such as TiO<sub>2</sub>, to EtOH at 300 K yields surface ethoxides. This is verified by comparison with reference spectra of surface alkoxides on TiO2<sup>16,22,33,45,61</sup> and of titanium(IV) ethoxide.<sup>26</sup> There, the strong O-H stretching and bending vibrations at 3675 and 1244 cm<sup>-1</sup> present in vapor phase EtOH (Figure 8b) disappear upon adsorption.<sup>16,22,33,45,61</sup> The lack of these bands in Figure 8a provides strong evidence for the formation of the surface alkoxide, since the O-H vibrations would be readily observed if the alcohol were bonded to the surface via a M-C linkage (where M represents a metal atom, in this case, Ti).<sup>61</sup> Furthermore, in comparing the vibrational features of the hydrocarbon backbone of the adsorbed species with the parent alcohol, we found that the  $\nu$ (C-H),  $\delta$ (C-H), and  $\nu$ (C-O) bands are essentially unchanged, and the line shape of the spectra (Figure 8a) strongly resembles that of  $Ti(OEt)_4$ <sup>26</sup> Based on these observations, the only possible surface species are molecular EtOH and adsorbed alkoxide.<sup>22,55</sup> No new vibrational features are observed upon adsorption of the alcohol;<sup>22</sup> in particular, no olefinic CH stretching (~3020 cm<sup>-1</sup>) or bending vibrations were present.<sup>45,46,62</sup> With no significant changes in the skeletal vibrational features, the adsorbed alkoxide must bond via the oxygen atom to the surface.<sup>61</sup> Previous studies of EtOH exposed rutile showed no preferential adsorption with surface hydroxyl groups, nor were there any significant differences in the IR spectra for EtOH deposited at room temperature or at 673 K.33 Adsorbed ethoxide is a stable species<sup>22,61</sup>at room temperature, since extended evacuation ( $\sim$ 36 h) did not result in any changes in the IR spectra.

### **IV.** Discussion

A. Dissociative Adsorption of TEOS on TiO<sub>2</sub>. In this section, we analyze the FTIR and TPD data, propose a detailed

mechanism for adsorption and decomposition of TEOS on a dehydroxylated TiO<sub>2</sub> surface, show that the surface species are ethoxide and monoethoxysilyl ligands, and summarize our findings in describing the nature of the silica network formed by decomposition of TEOS. Interpretation of the FTIR data follows the arguments of a previously published study of the adsorption and reactions of TEOS on amorphous silica, where Tedder et al. exposed amorphous silica to TEOS at 450 K and modeled the reactions by ethanol adsorption at the same temperature.<sup>16</sup> They found TEOS produced a surface species with a nearly identical IR spectra as the ethoxide species derived from dosing ethanol to the same surface.<sup>16</sup> Only the dissociative adsorption of TEOS to form surface ethoxide groups and silyl ligands could produce such IR spectra. Similarly, researchers probing the reaction of methyltrimethoxysilane (MTMSi) on dehydroxylated silica with IR found dissociative adsorption, yielding surface methoxy and  $MeSi(OMe)_2$  (where  $Me = CH_3$ ) groups.<sup>17,18</sup> On the amorphous silica surface, Tedder et al. found the TEOS-derived spectrum had ~2.25 times the IR intensity as that of EtOH,<sup>16</sup> and they concluded that a combination of di- and trisiloxanes, (SiO)<sub>2</sub>Si(OEt)<sub>2</sub> and (SiO)Si(OEt)<sub>3</sub>, were the most likely surface species.<sup>16</sup> At a saturation coverage these species would yield vibrational bands like those of an adsorbed ethoxide, but with 2 or 3 times the intensity compared to ethanol.16

In our first series of experiments, a dehydroxylated TiO<sub>2</sub> surface was exposed to  $1.1 \times 10^8$  langmuirs of EtOH, regenerated, and dosed with  $2.1 \times 10^8$  langmuirs of TEOS. The second set of experiments exposed TiO<sub>2</sub> to  $1.1 \times 10^8$  langmuirs of EtOH; the sample was regenerated and exposed to  $\sim 2.2 \times$ 10<sup>8</sup> langmuirs of H<sub>2</sub>O followed by  $\sim 2.4 \times 10^8$  langmuirs of TEOS. These room temperature exposures gave saturation coverages. A different sample was used in each series in order to examine only the interactions of EtOH and TEOS with the titanium dioxide substrate, with no buildup of SiO<sub>2</sub> from the decomposition of TEOS. These samples were then heated to 850 K (in intervals) and regenerated (see Figures 2 and 5). Upon adsorption of TEOS on either the dehydroxylated or water predosed surface, surface ethoxide groups and silyl ligands are formed. The presence of silyl ligands is verified by TPD, in which desorption of the parent molecule was negligible, and by FTIR, where the  $\nu(Si-O)$  peaks undergo only minimal intensity losses with extended evacuation or increasing heat treatment (Figure 2C). Evidence for the formation of surface ethoxide ligands is provided by the lack of any new peaks in the  $\nu$ (C-H) or  $\delta$ (C-H) regions with heating or extended evacuation, since no olefinic vibrations are observed. In addition, the major TPD products were binary carbon species and desorbed at similar temperatures and with the same peak shapes as products from the ethanol dosed surface. Finally, we know from our prior study of TEOS on  $TiO_2(110)$ .<sup>14</sup> and other similar studies, 4,6,13,15-20,56 that SCAs dissociate to surface alkoxide and silyl ligands. On the basis of both FTIR and TPD data, we find TEOS decomposition forms only surface ethoxide and silvl ligands; we do not observe any other intermediate reaction products.

**B.** Identification of Monoethoxy Silyl Ligand. We have measured the  $\nu(C-H)$  peak areas for the entire set of IR spectra of TEOS and EtOH (saturation exposure at room temperature) on TiO<sub>2</sub> as a function of temperature (Figures 2 and 5). The areas of the peaks, determined by a Gaussian curve-fitting routine, were used to compute the intensity ratio,  $I[\nu(C-H)_{TEOS}]$ :  $I[\nu(C-H)_{EtOH}]$ . The  $\chi^2$  value of the curve fits was typically  $<10^{-3}$ . A similar analysis of the  $\delta(C-H)$  region of the IR spectra verified the analysis presented here. Because the vibrational spectra were first obtained for the EtOH exposed samples and regenerated prior to TEOS exposure, the  $TiO_2$  substrate for the two adsorption/anneal series were nearly identical and were representative of clean  $TiO_2$  samples. Therefore, no other factors, such as sample surface area, were necessary to compute the intensity ratio.

The  $I[\nu(C-H)_{TEOS}]:I[\nu(C-H)_{EtOH}]$  intensity ratio of the adsorbed ethoxide species provides information about the stoichiometry of the surface silvl ligand.<sup>16</sup> In this work, we found TEOS adsorption on a dehydroxylated sample gives an average intensity ratio  $I[\nu(C-H)_{TEOS}]:I[\nu(C-H)_{EtOH}]$  of 1.26  $\pm$  0.27 over the temperature range 300-800 K. On the water predosed sample, we find the  $I[\nu(C-H)_{TEOS}]:I[\nu(C-H)_{EtOH}]$ intensity ratio is  $1.06 \pm 0.25$  over the same temperature range. In both cases, the intensity ratio decreased slightly with increasing temperature; in part, this is due to slightly less accurate curve fits of the smaller peaks (high temperature). The TiO<sub>2</sub> surface was exposed with saturation doses of TEOS and EtOH in order to maximize the number of ethoxide-surface site interactions. Since the intensity of the OEts vibrations are nearly identical on the TEOS exposed sample to those produced by a saturation exposure of EtOH throughout the temperature range studied, we deduce that the silvl ligand is a monoethoxy species of the form Si(OEt). In contrast, Tedder et al. found the  $I[\nu(C-H)_{TEOS}]$ :  $I[\nu(C-H)_{EtOH}]$  intensity ratio for TEOS and EtOH deposited on SiO<sub>2</sub> to be about 2, indicating a diethoxysilyl surface ligand.<sup>16</sup> Inherent in this argument is that the dissociation products react with the same number of surface sites. Recall that we have studied polycrystalline TiO<sub>2</sub> samples, where many crystal faces, each with different surface atom densities, are exposed during TEOS or EtOH doses. While the ethoxide groups probably interact with Ti surface cations, the silyl ligands most likely bond to surface oxygen atoms;<sup>14</sup> if each of the larger monoethoxysilyl ligands obstructs one Ti cation site from interacting with a free ethoxide group, the number of reactive surface sites is conserved. Therefore, saturation exposures of TEOS and EtOH to polycrystalline TiO<sub>2</sub> at 300 K produce a maximum number of ethoxide and monoethoxysilyl surface ligands.

C. Thermal Decomposition and Product Desorption from TEOS on TiO<sub>2</sub>. Examination of the TPD data provides further evidence for the monoethoxy surface silvl ligand. Recall that the TPD product distribution for the major desorption products from EtOH on TiO<sub>2</sub> (Table 4) is 1:1:2 low-temperature ethanol: high-temperature ethanol:high-temperature ethylene. Ethylene production in the high-temperature regime is known to proceed primarily by  $\beta$ -hydrogen elimination.<sup>14,22,29,43</sup> Additionally, we know that the surface silvl ligand is stable to  $\sim 650 \text{ K}^{14,17,18}$ and that the desorption and reaction probability of the ethoxide ligands is not significantly altered by neighboring Si atoms or surface silvl ligands. Evidence for the invariant reactivity of ethoxide groups in the presence of Si was obtained by repeatedly exposing a TiO<sub>2</sub> sample to EtOH, heating to 1000 K, regenerating the sample, exposing it to TEOS, heating to 1000 K to form SiO<sub>2</sub>, and regenerating the sample. Even after several cycles, the relative product yield in TPD spectra, following adsorption of EtOH or TEOS, was nearly identical to that from a fresh sample (Figures 3 and 6). In addition, the IR spectra were indistinguishable from those shown in Figure 7 and 8, except for the silica-like peak at  $1040 \text{ cm}^{-1}$ . Had the reactivity of the ethoxide groups changed in the presence of Si, we would have seen consistent changes in the TPD and FTIR spectra with the number of cycles, in which SiO<sub>2</sub> was continually built up on the surface.

As shown in Table 2, the major products desorbing from a TEOS exposed  $TiO_2$  surface are ethanol and ethylene, with the low-temperature state comprised primarily of ethanol. Ethoxide

ligands bound to Si and to Ti have different desorption behavior, which can be observed in the TPD spectra. We have modeled the predicted TPD product yields for mono-, di-, and triethoxysilyl ligands based upon a constant number of surface sites for attachment of ethoxy ligands. (The model accounted for site blocking by the silvl ligand, as well.) The only model which was consistent with the data is for detachment of three OEt ligands and the formation of a monoethoxysilyl moiety upon dissociative adsorption of TEOS on this surface. The lowtemperature desorption state accounts for  $\sim 20-25\%$  of all desorption products; we observe a corresponding decrease of ~25% in the  $\nu$ (C–H) and  $\delta$ (C–H) peak areas. Upon heating to >650 K, the only carbon-containing species we observe desorbing are ethanol and ethylene in a  $\sim$ 1:2 ratio, while the corresponding IR peak intensity in the  $\nu$ (C-H) and  $\delta$ (C-H) regions disappears. Since we know the TPD product yield and we know that the monoethoxysilyl ligand decomposes to SiO<sub>2</sub> and vapor phase products in the high-temperature range, we can conclude that the silvl ligand also produces ethanol and ethylene in a 1:2 ratio. The overall TPD product distribution for TEOS on TiO<sub>2</sub> is  $\sim$ 1:1:2 low-temperature ethanol:hightemperature ethanol:high-temperature ethylene, based on a total of four desorption products (i.e., the reaction of four ethoxy ligands per TEOS parent molecule).

On the water predosed  $TiO_2$ , we also observe dissociative adsorption of TEOS to form surface ethoxides and monoethoxysilyl species. TPD from the water predosed surface yields an overall product distribution (based on four desorption products) of  $\sim$ 1:2:1 low-temperature ethanol:high-temperature ethanol: high-temperature ethylene (Table 3). We observe an IR peak area loss of  $\sim 20-25\%$  on heating a water and TEOS exposed sample through the first desorption state (>450 K), corresponding well with the TPD analysis. However, in the hightemperature state, the TPD product distribution varies from that of an ethanol dosed sample. In contrast to the TEOS interaction on a dehydroxylated TiO<sub>2</sub>, the water predose provides some hydroxyl groups on or near the surface at higher temperature.<sup>25,30,31,33</sup> (We found water desorbed from this surface at  $\sim$ 400 K with an extensive tail to  $\sim$ 550 K and some minor desorption even as high as ~650 K.) These hydroxyl groups react effectively with the surface ethoxide groups to desorb as ethanol, at the expense of the  $\beta$ -hydrogen elimination reaction producing ethylene. Previously, we observed a shift of product distribution from the high-temperature state to the lowtemperature state upon TEOS adsorption on a water predosed TiO<sub>2</sub> single crystal. In this study, we have used different polycrystalline samples for the various experiments, and we cannot determine absolute TPD peak areas (without extensive effects, such as sample mass) to quantitatively compare desorption from the dehydroxylated and water predosed polycrystalline TiO<sub>2</sub> surfaces.

**D.** Silica Network Formation. FTIR, as well as TPD, allows us to study TEOS decomposition on this  $TiO_2$  surface in great detail. In aggregate, the frequencies, line shapes, and temperature dependencies of the IR peaks at 3740 and 1040 cm<sup>-1</sup> offer strong evidence for the formation of a siloxane or silica-like network structure. It is well-known that an infinite siloxane chain will almost entirely fill the absorption region between 1111 and 1000 cm<sup>-1</sup>, with maxima occurring at ~1087 and 1020 cm<sup>-1</sup> in the IR spectrum.<sup>28</sup> In addition, Si–O vibrations are observed at ~1050 cm<sup>-1</sup> in methyl polysiloxanes and for the degenerate symmetric vibrations of the SiO<sub>4</sub> group in liquid siloxanes,<sup>35</sup> while vibrations between ~1020 and 1080 cm<sup>-1</sup> are also observed for siloxane bonds in tri-, tetra-, and pentasiloxane rings where the peak position depends upon ring strain.<sup>28,36</sup> This band in polysiloxanes corresponds to the

vibration at  $\sim 1100$  cm<sup>-1</sup> found in all forms of silica.<sup>37</sup> Reference spectra of silica<sup>26</sup> show a strong band at 1106 cm<sup>-1</sup> with a peak shape strikingly similar to that found in Figures 1C and 2C. In addition, the behavior of the peak at  $3740 \text{ cm}^{-1}$ on the water predosed surface also provides strong evidence for the formation of siloxane or Si-O ring structures. As seen in Figure 2B, as the sample was heated above 750 K, the intensity of the  $\nu(Si-OH)$  peak decreased and then nearly doubled in intensity after the regeneration procedure. The former behavior for isolated hydroxyl groups on silica has been observed previously in conjunction with the formation of strained Si-O rings,<sup>53,54</sup> where the population of strained Si-O ring structures increased with heat treatment. These authors verified the formation of polymeric-like siloxane structures by a detailed examination of peaks at 908 and 888  $cm^{-1}$ , characteristic of the strained  $\nu$ (Si-O) vibration.<sup>53,54</sup> Others have noted the dehydroxylation of a high surface area SiO<sub>2</sub> powder at increasing temperatures leads to an increase in intensity of the strained  $\nu(Si-O)$  IR peaks, which correlate well with changes at  $\sim$ 3740 cm<sup>-1</sup>, the isolated OH vibration.<sup>64,65</sup> Primarily, a low-frequency shoulder on the  $\nu$ (Si-OH) peak decreases with increasing anneal temperature, due to loss of hydrogen-bonded hydroxyl groups.<sup>64,65</sup> In addition, the isolated hydroxyl stretch was observed at a lower frequency upon rehydroxylation of SiO<sub>2</sub> compared to the  $\nu$ (Si-OH) vibration on a native oxide.<sup>64,65</sup> Annealing of SiO<sub>2</sub> films is often regarded as an ordering process which increases long-range order and crystallinity.<sup>51</sup> Since TiO<sub>2</sub> is opaque at low frequencies, we were unable to directly examine the SiO<sub>2</sub> modes at 908 and 888  $\text{cm}^{-1}$ ; however, the temperature dependence, peak shapes, and positions of the peaks at 3740 and 1040 cm<sup>-1</sup> strongly suggest the formation of silica networks upon reaction of TEOS on TiO<sub>2</sub>.

The mechanism of forming SiO<sub>2</sub> from the decomposition of TEOS on TiO<sub>2</sub> leads to a silica network, grouped in clusters or islands. It is known that the characteristic vibrational modes of SiO<sub>2</sub> occur at frequencies  $50-100 \text{ cm}^{-1}$  lower for films that are less than 50 Å thick<sup>20</sup> and that the  $\nu$ (Si-O-Si) vibrational band at  $\sim 1100 \text{ cm}^{-1}$  shifts to lower frequency for silica gels with more "open" structures.<sup>39</sup> The position of the  $\nu(Si-O)$ peak in our study (Figures 1C and 2C) indicates an "open" silica network structure or one in which Si-O-Si ring structures are not highly interlinked. In addition, others have found that the degree of interlinking in a polymeric siloxane network is determined by the quantity of EtOH evolved in the decomposition process.<sup>48,50</sup> On the water predosed surface, we observed a relatively greater amount of EtOH produced in the hightemperature state (Tables 2 and 3), at the expense of ethylene production, demonstrating that the silica network is cross-linked to a higher degree when water is predosed. Previously, we observed about twice the amount of TEOS reacted on the water predosed TiO<sub>2</sub> single-crystal surface than on the dehydroxylated surface;<sup>14</sup> in this study, we observe the 1040 cm<sup>-1</sup> peak is about 2 times as intense when TEOS is exposed to a water predosed surface than a dehydroxylated TiO<sub>2</sub> sample. Although this may qualitatively indicate that more TEOS reacts when the surface is predosed with water, exposures and peak intensities could not be corrected for sample surface area, and an absolute comparison could not be made. Whether or not water is predosed, the resulting SiO<sub>2</sub> network does not uniformly cover the surface. Our prior study of the adsorption and reactions of TEOS on a  $TiO_2(110)$  single crystal<sup>14</sup> showed that the resulting SiO<sub>4</sub> tetrahedra formed upon heating the TEOS exposed surface to >650 K were clustered into tall, three-dimensional islands. Previous studies of TEOS decomposition on a series of polycrystalline metal oxides, including TiO<sub>2</sub>, found that decomposition of the SCA on polycrystalline TiO<sub>2</sub> formed clusters of silica species, covering not more than 70% of the surface.<sup>4,12</sup> Our current investigation showed that upon repeatedly reacting TEOS, heating, and regenerating the same sample, additional SiO<sub>2</sub> was deposited as evidenced by increasing IR intensity at 3740 and 1040 cm<sup>-1</sup>; yet, peak positions and relative intensities of IR and TPD features for EtOH, water, and TEOS adsorption were unchanged on these surfaces. The reactivity of the surface is not affected by the formation of silica networks deposited by repeated cycles of TEOS adsorption, indicating that bare substrate sites are available for further TEOS decomposition.<sup>4,12</sup> Previously,<sup>14</sup> we observed decreased reactivity of a TiO<sub>2</sub>(110) single crystal with increasing cycles of TEOS exposure and annealing. Therefore, since we have no evidence for desorption of either SiO<sub>2</sub> or molecular TEOS, the silica networks must be clustered into islands or diffuse into the bulk to form solid solutions of mixed oxides, leaving some TiO<sub>2</sub> sites uncovered and available for additional reaction with TEOS.<sup>4,12,14</sup> On the basis of our prior XPS studies of TEOS on a TiO<sub>2</sub>(110) singlecrystal surface<sup>14</sup> and the FTIR results presented here, we believe the silica networks to be grouped in large, three-dimensional islands on the surface; when water is predosed, the resulting SiO<sub>2</sub> structures are interlinked to a greater degree.

**E. Reaction Mechanism.** 1. TEOS Decomposition on Dehydroxylated  $TiO_2$ . On the basis of the evidence presented above, we propose the following reaction mechanism for TEOS adsorption and decomposition on a dehydroxylated  $TiO_2$  surface. (The subscript s represents a surface ligand.) The TEOS shown in reaction 1 reacts with a surface site, most likely an oxygen atom in the  $TiO_2$  lattice or one of the minority OH<sub>s</sub> groups not removed by the surface oxidation procedure. Ethoxy ligands likely bind to Ti cation sites. The nature of the reactant H\* in reaction (1) will be addressed below.

300 K: 
$$TEOS + H^* \rightarrow Si(H)OEt_s + 3OEt_s$$
 (1)

450 K: 
$$Si(H)OEt_s + OEt_s \rightarrow EtOH_g + SiOEt_s$$
 (2)

650 K: 
$$2OEt_s \rightarrow C_2H_{4,g} + EtOH_g + O_s$$
 (3)

$$O_s + SiOEt_s \rightarrow SiO_{2,s} + C_2H_{4,g} + \frac{1}{2}H_{2,g}$$
 (4)

net: 
$$\text{TEOS} + \text{H}^* \rightarrow 2\text{EtOH}_g + 2\text{C}_2\text{H}_{4,g} + \text{SiO}_{2,s}$$
 (5)

Hydrogen produced in reaction 4 may go to the gas phase or be readsorbed in the form of minority OH<sub>s</sub> groups on the surface; however, since TPD data are not quantitative for m/e = 2, hydrogen is not considered a net product in reaction 5. Reaction 3 is a known  $\beta$ -hydrogen elimination reaction, shown previously to occur at this same temperature for ethoxide decomposition on TiO<sub>2</sub>.<sup>22,29,43</sup> We previously observed the same net reaction with the same products as in reaction 5 for TEOS decomposition on a dehydroxylated TiO<sub>2</sub>(110) single crystal.<sup>14</sup> Products due to ethoxide decomposition in reactions 2 and 3 are consistent with the TPD product distribution and IR heat treatment series of ethanol exposed TiO<sub>2</sub>. The source of the hydrogen which appears in reaction 1 as H\* is evidenced by the  $\nu(Si-H)$ vibration at  $\sim$ 2207 cm<sup>-1</sup> in Figure 7a and is not understood at this time. It may arise from the displacement of the hydroxylic hydrogen atom of minority surface hydroxyl groups to the silyl ligand. Without the contribution of this hydrogen atom to the surface silyl ligand in reaction 1, we expect no low-temperature desorption of ethanol or other products. Then, the reaction would proceed as we previously observed on the dehydroxylated TiO<sub>2</sub>(110) single crystal,<sup>14</sup> where equal quantities of EtOH and  $C_2H_4$  desorbed only at 650 K. Recall that the IR intensity ratio,  $I[\nu(C-H)_{TEOS}]$ :  $I[\nu(C-H)_{EtOH}]$  was slightly greater than one for TEOS exposures to a dehydroxylated, polycrystalline  $TiO_2$  surface; therefore, some diethoxysilyl ligands may be formed as TEOS decomposes in reaction 1. These diethoxysilyl ligands still produce network  $SiO_2$  as they can further decompose on the surface to the monoethoxysilyl surface species and follow the chemistry presented above.

2. TEOS Decomposition on Water Predosed TiO<sub>2</sub>. In contrast, many hydroxyl groups are available to react with TEOS on the water predosed polycrystalline TiO<sub>2</sub> surface. In this case, IR spectra (Figure 7b) show that most of these hydroxyl groups are hydrogen bonded and are apparently readily accessible for interaction with TEOS. Thus, TEOS reacts on water predosed TiO<sub>2</sub> as follows.

300 K: 
$$TEOS \rightarrow SiOEt_s + 3OEt_s$$
 (6)

$$450-550 \text{ K: OH}_{s} + \text{OEt}_{s}$$

 $EtOH_g + O_s$  (occurs three times) (7)

650 K: 
$$2O_s + SiOEt_s \rightarrow SiO_2(OH)_{network} + C_2H_{4,g}$$
 (8)

net: 
$$TEOS + 2OH_s + O_s \rightarrow 3EtOH_g + C_2H_{4,g} + SiO_2(OH)_{network}$$
 (9)

Again, the net reaction, reaction 9, is the same as what we observed on the water predosed TiO<sub>2</sub> single crystal,<sup>14</sup> except on polycrystalline TiO<sub>2</sub> one of the hydroxyl groups is retained as SiOH, as indicated in reaction 8. Initial adsorption of TEOS on the water predosed surface, reaction 6, differs from that on the dehydroxylated surface, reaction 1, because the surface OH groups are strongly hydrogen bonded and the hydroxylic hydrogen atom is not displaced by the silvl ligand. The ethoxide groups formed in reaction 6 combine with the surface OH to form EtOH. Ethanol then desorbs at 450 K as in reaction 7. Reaction 7, which occurs twice at  $\sim$ 550 K, is expected because OH groups are known to remain on TiO<sub>2</sub> to temperatures as high as  $\sim 1000$  K;<sup>31</sup> ethoxide ligands combine with these hydroxyl groups to form gas phase EtOH. As we showed previously,<sup>14</sup> on the water predosed TiO<sub>2</sub>(110) surface, the reaction of OH and OEt groups to form molecular ethanol allows additional TEOS to dissociate in the low-temperature regime. We cannot directly compare TEOS exposures to the dehydroxylated and water predosed surfaces in this study since new samples with different absolute surface areas were used for each experiment in order to examine only the reactions of TEOS with  $TiO_2$  (i.e., to avoid interaction with the SiO<sub>2</sub> films built up after extended reaction). However, the IR and TPD data do indicate that a water predose to polycrystalline TiO<sub>2</sub> yields greater relative desorption of EtOH in the low-temperature state (in turn, possibly creating more free sites for TEOS adsorption and decomposition at 450 K) and produces silica networks interlinked to a greater degree than on the dehydroxylated surface. Reactions 4 and 8 show that formation of the SiO<sub>2</sub> network begins at  $\sim 650$  K with the liberation of ethylene to the gas phase. Some of the sites in the SiO<sub>2</sub> network are hydroxylated as indicated by the SiO(OH) species shown in reactions 8 and 9.

#### V. Conclusion

We have exposed dehydroxylated and water predosed polycrystalline  $TiO_2$  to TEOS. At 300 K, TEOS dissociatively adsorbs on the dehydroxylated or water predosed surfaces, forming a monoethoxysilyl surface species and ethoxy ligands. The ethoxy groups decompose in the range 450-650 K to form gas phase ethylene and ethanol, just as they do on an ethanoltreated TiO<sub>2</sub> surface. The monoethoxysilyl ligand decomposes at 650 K to evolve vapor phase ethylene and a silica network. The vapor phase product distribution is 1:1:2 low-temperature ethanol:high-temperature ethanol:high-temperature ethylene on the dehydroxylated surface and is 1:2:1 on the water predosed surface. The silica network is characterized by an IR peak at 1040  $cm^{-1}$ ; on the water predosed surface, we also observe a peak at 3740 cm<sup>-1</sup>, indicative of isolated hydroxyl groups on SiO<sub>2</sub>. The temperature dependence of the  $\nu$ (Si–OH) peak at 3740 cm<sup>-1</sup> indicates that the silica network formed by decomposition of TEOS on the water predosed surface is interlinked to a greater degree and is composed of siloxane ring structures. The work presented here both supplements and complements our prior study of TEOS adsorption and decomposition on a TiO<sub>2</sub>(110) single crystal. In addition, this investigation is relevant to understanding of the fundamental surface interactions and reaction mechanisms of SCAs with oxide surfaces.

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